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Mn^{2+} centers in ZnS:Mn Thin-film EL Device Active Layer

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Synopsis

It is very important to understand the state of incorporated Mn^{2+} centers to fabricate bright ZnS:Mn thin-film electroluminescent (TFEL) devices. As the concentration of Mn is much less than that of ZnS, it is very difficult to investigate its influence on luminescence. Five kinds of ZnS:Mn active layers with different Mn concentration were fabricated by RF magnetron sputtering method, and X-ray photoelectron spectroscopy (XPS) and Photoluminescent (PL) spectrum were examined to determine Mn $3d$ orbit level and to decide the preferable weight percentage of Mn. Mn $3d$ orbit level were 2.6 eV and 4.7 eV below vacuum level, and 0.5 wt. % was most efficient.

Keywords: Electroluminescence, ZnS:Mn, Sputtering, XPS, Photoluminescence

1. Introduction

Alternating current TFEL devices have been investigated as one of the hopeful flat-panel displays because of the advantages such as completely solid state, emissive display with wide viewing angle and rapid response time. Among the TFEL device fabrication methods such as sputtering[1)], electron-beam (EB) deposition, metal organic chemical vapor deposition (MOCVD) and atomic layer epitaxy (ALE), we selected sputtering method. The sputtering method is a convenient fabrication method which enables large area device fabrication at low cost. In this study, we fabricated five kinds of active layers on the substrate and investigated the state of incorporated Mn^{2+} centers.

2. Device fabrication and experimental

ZnS:Mn active layer was fabricated on indium-tin-oxide (ITO)(MATSUNAMI GLASS IND., Corning #7059) coated glass substrate by RF magnetron sputtering method. Sputtering target was prepared in the following procedures. ZnS powder (5N, 300 mesh, FURUUCHI CHEMICAL CORPORATION) and MnS powder (2N, KOJUNDO CHEMICAL LABORATORY CO.,LTD.) were mixed together and fired at 550 °C in an argon atmosphere for 4 hours. There are two types of crystal structures, zincblende-type and wurtzite-type. Films used in this study were zincblende-type, shown in Fig. 1. It is known that a wurtzite-type structure is obtained when annealed at a temperature higher than 1100 °C.

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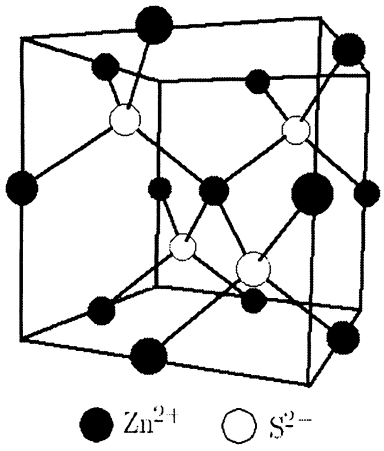

Fig. 1: Zincblende crystal structure of ZnS

Table 1: Deposition conditions

Target	ZnS+MnS powder
Base pressure	1.2×10^{-6} Torr
Gas pressure	2.0×10^{-3} Torr
Sputtering gas flow rate	Ar (10 ccm) + He (10 ccm)
Deposition time	50 min.
Substrate temperature	200 ℃
RF power	50 W
Annealing temperature	200 ℃
Annealing time	40 min.

Table 1 shows the deposition conditions. The following five kinds of active layers were prepared using different sputtering targets: (a)active layer prepared with ZnS powder without Mn, (b)active layer prepared with ZnS powder with 0.5 wt. % Mn, (c)active layer prepared with ZnS powder with 1.0 wt. % Mn, (d)active layer prepared with ZnS powder with 2.0 wt. % Mn and (e)active layer prepared with ZnS powder with 20.0 wt. % Mn. Figure 2 and Table 2 shows the X-ray diffraction(XRD) patterns and thickness of the samples, respectively. Though the sputterings were performed under the same conditions, the thickness of each sample was not the same. It would probably be due to the difference in sputtering yields of ZnS and MnS.

The usual structure of ZnS:Mn EL device is /Glass substrate/ITO/Insulating layer/ZnS:Mn(Active layer)/Insulating layer/Al electrode/. However in this study, the deposition of insulating layer and electrode was not performed, because we are interested just in the investigation of the state of Mn^{2+} centers in active layer by XPS and PL method.

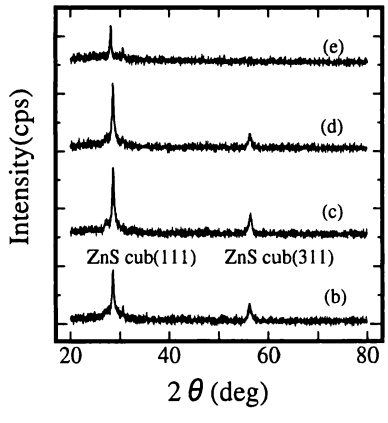

Fig. 2: XRD patterns

Table 2: Thickness of active layer

Active layer	Thickness(Å)
(b)	15000
(c)	12900
(d)	8700
(e)	2700

Table 3: XPS analysis conditions

Start Energy	15 eV	Sampling Time	1.0 sec
Stop Energy	0 eV	Repeat Time	10 times
Step Energy	0.05 eV	X-ray Source	Mg

XPS spectra were obtained by X-ray photoelectron spectroscopy(ESCA-750, SHIMADZU CORPORATION) and data processing system(ESPAC100, SHIMADZU CORPORATION). As ZnS:Mn EL peak wavelength is 585 nm due to the Mn^{2+} $3d$ levels, we decided to analyze the valence band region of the samples and decided the Mn^{2+} levels below vacuum level. Table 3 shows analysis conditions. We

performed XPS investigation only on samples (a) without Mn and (e) with the highest concentration of Mn.

Figure 3 shows a PL spectrum measurement system. PL spectrum was measured as follows[2]. A 150 W Xenon lamps (WACOM R&D CORPORATION, Model XD-151S) was used as an excitation source. The light of the Xenon lamps through two glass filters (HOYA U-340, U-360) and interference filter (334.0 nm) was chopped into 275 Hz signal with an optical chopper (SCITEC INSTRUMENTS). Figure 4 shows the incident light. PL under the excitation light was monochromized and transformed into an electric signal by a combination of a monochromator (JASCO, Model CT-25C) and photomultiplier (HAMAMATSU, Model R1387). The electric signal was fed to a lock-in amplifier (NF, Model LI-572B) and synchronized with the reference signal of optical chopper. At last the electric signal data was acquisited through an A/D converter (Interface, Model IBX-3120) and analyzed by a personal computer. We measured PL spectra of samples (b), (c), (d), (e), and four kinds of powder. When we measured powder PL, the same mass of powder placed on the ITO glass was examined.

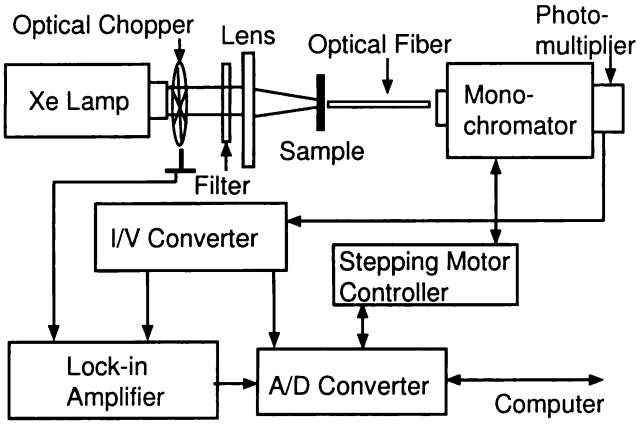

Fig. 3: Spectrum measurement system

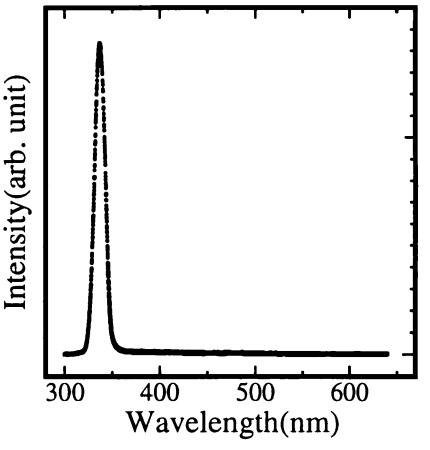

Fig. 4: The excitation light for PL measurement

3. Experimental results and discussion

3.1 Analysis of valence band of ZnS:Mn by XPS method

Figure 5 shows XPS spectra of two samples (a) and (e) after charging, smoothing and background correction. Because the differences of two spectra are caused by the existence of Mn, we can find out the levels of Mn from these spectra. To find them, peak separation of the spectrum was performed with least squares method assuming Gaussian peaks. To solve least squares problem, we used a FORTRAN program generated by ASNOP (Application System for Nonlinear Optimization Programs)[3]. ASNOP is an application system which generates a FORTRAN program automatically.

Firstly, we separated spectrum of sample (a) into four peaks (dotted line), as shown in Fig. 6. Secondly, we separated spectrum of sample (e) into six peaks, the previous four peaks (dotted line) and other two more peaks(solid line) as shown in Fig. 7. Dashed lines in Fig. 6 and Fig. 7 are measured data. These two peaks at 2.6 eV and 4.7 eV below vacuum level are the levels of Mn^{2+} $3d$ orbit, and electrons transit from 2.6 eV level to 4.7 eV level on EL emission. The energy difference corresponds to the wavelength of 590 nm which, is pretty close to the EL peak wavelength of 585 nm.

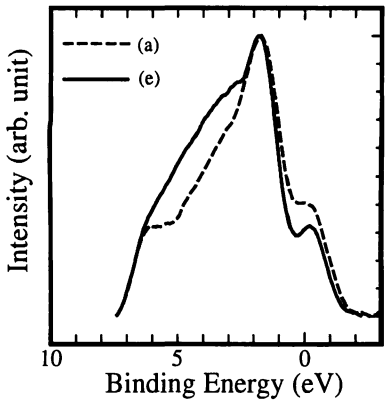

Fig. 5: XPS Spectrum of valence band

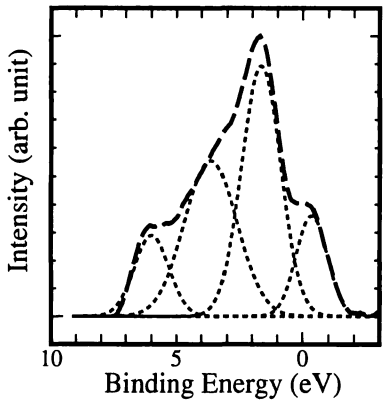

Fig. 6: Peak separation of sample (a) XPS spectrum

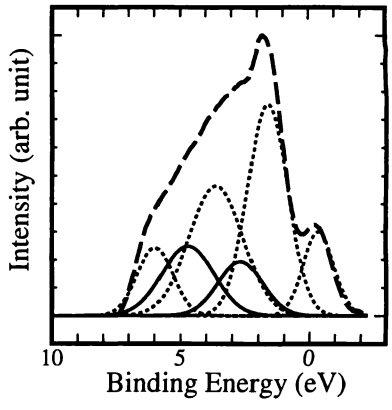

Fig. 7: Peak separation of sample (e) XPS spectrum

3.2 The measurement of PL intensity

Figure 8 and 9 show the PL spectra of the thin films and powder, respectively. In the case of thin film, the luminance decreased with increasing Mn concentration and sample (e) showed no emission. These PL intensity were the original value divided by each thickness at the concentration region examined. PL dependence and EL dependence on the Mn concentration is the same. It suggests that we can use PL investigation for optimizing EL device active layer. On the other hands, powder PL showed quite opposite results. That is, PL intensity increases with increasing Mn concentration up to 20 wt. %. Probably, Mn^{2+} state in the thin film is considerably different from that in the powder. It is expected that much more isolated Mn^{2+} exist in the powder than in the thin film.

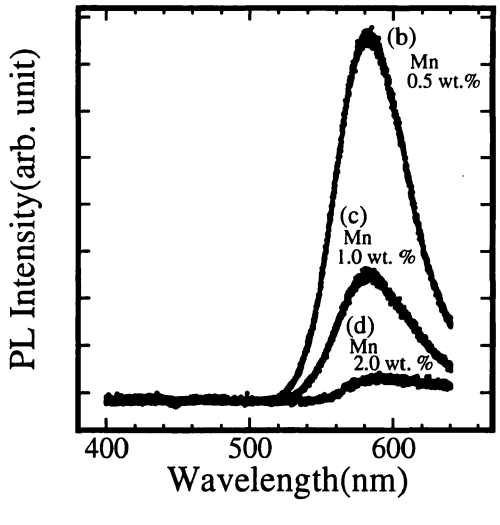

Fig. 8: PL spectra of thin film

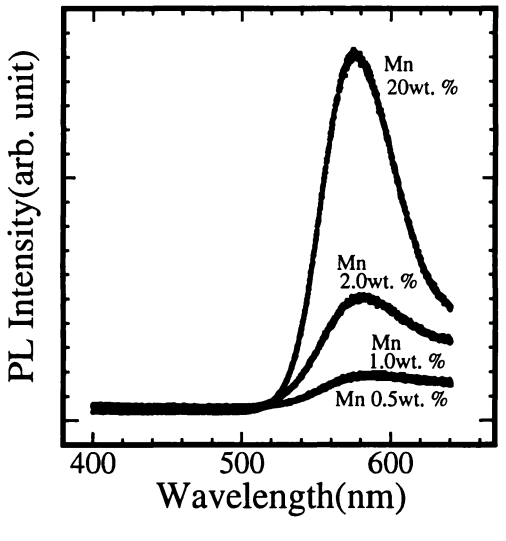

Fig. 9: PL spectra of powder

4. Conclusion

The conclusions can be summarized as follows:

- Mn^{2+} $3d$ levels were estimated to be 2.6 eV and 4.7 eV below vacuum level. The enegy difference between two levels of 2.1 eV corresponds to wavelength of 590 nm, which is very close to the EL emission wavelength of 585nm.
- PL of thin film decreased with increasing Mn concentration, but PL of powder increased with increasing Mn concentration up to 20 wt. %.
- The fact that many isolated Mn^{2+} can exist in the powder up to 20 wt. % suggests that such high concentration of isolated Mn^{2+} can be realized also in thin film. And if some effective energy transfer mechanism is introduced, very efficient device would be fabricated.

5. References

1) M. Aozasa, et al., *Japanese Journal of Applied Physics*, **29**, 1997 (1990)

2) N. Tanimoto, et al., *Memoirs of Faculty of Engineering, Osaka City University*, **42**, 11 (2001)

3) I. Tsuda, et al., *Memoirs of Faculty of Engineering, Osaka City University*, **41**, 13 (2000)

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